sequence of the increased electron density in the inner ring due to the increase of nuclear charge. The comparable shift of positive charge from the outer to the inner ring of atoms, in the transformation of borazine to boroxine, due to replacement of alternate N–H by O atoms, also leads to a contraction [B–N = 1.435 Å to B–O = 1.376 Å] by exactly the same magnitude, 0.059 Å. However, a redistribution of charge within the ring has the opposite effect. One may imagine the conversion of benzene to borazine by the transfer of protons from alternate carbons to their neighbors. The ring expands by 0.038 Å on a side. The similar nuclear transformation from $H_3C_3N_3$ to $H_3B_3O_3$ has the identical effect. The increase in bond polarity within the rings and associated lowering of the π-electron delocalization by the increase in positive charge at three centers reduce the bond order. A quantitative analysis of the changes in ring dimensions and internal angles remains a worthwhile undertaking.

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Borane Cations of Base Oxides

BY N. E. MILLER

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A new class of borane cations with mixed bases is presented containing the oxide bases pyridine N-oxide, trimethylamine N-oxide, trimethylphosphine oxide, and dimethyl sulfoxide. These cations are considerably less stable toward basic hydrolysis than the corresponding cations without oxygen.

It is becoming increasingly clear that the $(base)BH_2{}^+$ grouping is a strong acid toward a variety of base sites. A striking example was recently presented in the synthesis of $H_2B(base)_2{}^+$ borane cations with amides bonded through the oxygen of the amide base.[1] Because of the unexpected stability of the cations with weak amide bases, exploration for cations with oxide bases was made and a new class of cations was demonstrated, namely, $(CH_3)_3NBH_2O(base)^+$ where the base is pyridine, trimethylamine, trimethylphosphine, or dimethyl sulfide.

Experimental Section

Practical grade pyridine oxide was rendered anhydrous by sublimation under vacuum at 70°. Trimethylphosphine oxide was prepared from phosphorus oxychloride and methylmagnesium chloride in ether by the method of Burg and McKee.[2] Trimethylamine oxide was prepared according to the method of Hickinbottom.[3] Dimethyl sulfoxide of commercial reagent grade quality was employed without additional purification. Trimethylamine–iodoborane was prepared from iodine and trimethylamine–borane in benzene by the method outlined by Ryschkewitsch and Garrett.[4] Anhydrous chloroform was obtained by distillation from phosphoric anhydride.

Preparation of Cations.—An equimolar amount of trimethylamine–iodoborane in anhydrous chloroform was added rapidly *via* syringe to a solution of the base oxide in chloroform. First contact of the solutions produced an orange coloration that persisted after completion of the addition with all the base oxides but trimethylamine N-oxide. The coloration instantly faded on contact of the solution with air. Solvent was removed after about 1 hr of standing, and the residues were taken up in water. Saturated ammonium hexafluorophosphate solution was added, precipitating the borane cations as the hexafluorophosphate salts. The hexafluorophosphates were recrystallized from acidified hot (about 60–90°) water. Yields were better than 80%.

Rapid handling of the salts of the cation with dimethyl sulfoxide base was required since the iodide and the crude hexafluorophosphate turned a dark orange and softened when left in contact with air. This behavior appears to be a decomposition reaction that probably involves oxygen and is catalyzed by the iodide ion. Recrystallized hexafluorophosphate salt left in the open for days did not discolor, but it slowly decomposed, releasing dimethyl sulfoxide.

Analyses and spectral data for recrystallized samples are collected in Tables I and II.

Hydrolysis.—The hydrolysis apparatus was a 15-ml flask, with a magnetic stirring bar, that was attached to a small gas buret.[5] A 3–10-mg sample of salt was dissolved in a precise quantity of 1.00 *M* potassium chloride contained in a 10-ml volumetric flask. The requisite amount of 1.00 *M* sodium hydroxide was added, the volume was adjusted to 10.0 ml, and the solution was transferred to the reaction vessel along with a small amount of powdered borosilicate glass. Rapid stirring in the presence of the powdered glass ensured uniform gas evolution. Graphical analysis of the data ($V_\infty - V_t$ *vs.* time) yielded the pseudo-first-order rate constants.

All of the borane cations in solution were rapidly degraded by strong base somewhere between room temperature and 100°.

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[1] N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R. Lundberg, *Inorg. Chem.*, **8**, 862 (1969).

[2] A. B. Burg and W. E. McKee, *J. Am. Chem. Soc.*, **73**, 4590 (1951). Attempts were made to use methylmagnesium bromide as the Grignard reagent with no success. Yields similar to those reported were obtained with methylmagnesium chloride.

[3] W. J. Hickinbottom "Reactions of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1962, p 420.

[4] G. E. Ryschkewitsch and J. M. Garrett, *J. Am. Chem. Soc.*, **89**, 4240 (1967).

[5] A detailed description of the technique is to be published in relation to the hydrolysis of another borane cation.

TABLE I

ANALYSES

Compound	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% B Calcd	% B Found
$(CH_3)_3NBH_2ONC_5H_5$	95–96	30.8	31.2	5.2	5.6	9.0	9.2	3.5	3.3
$(CH_3)_3NBH_2ON(CH_3)_3$	155 dec	24.4	24.8	6.8	7.0	9.5	9.9	3.7	3.8
$(CH_3)_3NBH_2OP(CH_3)_3$	142–142.8	23.3	23.5	6.5	6.8	4.5	5.1	3.5	3.5
$(CH_3)_3NBH_2OS(CH_3)_2$		20.4	20.2	5.8	5.5	4.8	5.9		

TABLE II

SPECTRAL DATA

Compound	Proton resonances[a]	Infrared absorption[c]
$CH_3)_3NBH_2ON(CH_3)_3{}^+PF_6{}^-$	NCH_3, 2.60 $ONCH_3$, 3.41	2400 m, 2330 w, 1410 w, 1255 m, 1220 m, 1180 m, 1130 m, 1115 w, 995 m, 850 s, b
$CH_3)_3NBH_2ONC_5H_5{}^+PF_6{}^-$	NCH_3, 2.73 C_5H_5N, 8.0–8.8[b]	3140 m, 2450 m, 2310 w, 1255 m, 1160 s, 1110 w, 1000 m, 960 w, 885 s, 845 s, 785 m, 680 m
$(CH_3)_3NBH_2OP(CH_3)_3{}^+PF_6{}^-$	PCH_3, 1.89 (J_{PCH} = 13 cps) NCH_3, 2.58	2410 m, 2330 w, 1495 m, 1305–1320 multiplet, m, 1255 m, 1220 m, 1180 m' 1090 s, b, 1020 m, 1000 m, 970 m, 850 s, b
$(CH_3)_3NBH_2OS(CH_3)_2{}^+PF_6{}^-$	SCH_3, 3.15 NCH_3, 2.61	2420 m, 2320 w, 1290 m, 1330 w, 1305 m, 1205 m, 1175 s, 1130 m, 1100 w, 1040 m, 1000 s, 960 m, 930 s, 850 s

[a] Chemical shifts in ppm downfield from internal tetramethylsilane for methylene chloride solutions. [b] The pyridine resonance was split greater than usual. [c] In cm^{-1}. Compounds were run as mineral oil mulls on a Perkin-Elmer 237B spectrometer. Only major bands are listed and characterized as w = weak, m = moderate, s = strong, b = broad.

TABLE III

HYDROLYSIS RATES (29.9°)

Compound	$[OH^-]$,[a] M	Rate,[b] sec^{-1}	Rate/$[OH^-]^2$, sec^{-1} M^{-2}
$(CH_3)_3NBH_2OP(CH_3)_3{}^+PF_6{}^-$	0.7	$3.9 \pm 0.1 \times 10^{-3}$ [c]	7.95×10^{-3}
	0.5	$1.89 \pm 0.03 \times 10^{-3}$	7.6×10^{-3}
	0.3	6.9×10^{-4}	7.65×10^{-3}
$(CH_3)_3NBH_2ON(CH_3)_3{}^+PF_6$	0.9	2×10^{-6}	
$(CH_3)_3NBH_2OS(CH_3)_2{}^+PF_6{}^-$	0.1, 0.2	(Half-life 60 sec[d])	

[a] Hydrolyses in solutions of 0.9 ionic strength, with potassium chloride as the other electrolyte. [b] Pseudo-first order rate in large excess of hydroxide. [c] Indicated uncertainty based on duplicate results. [d] Same curves obtained for 0.1 and 0.2 M hydroxide. Data fit first-order better than second-order rate. A pronounced curvature in the first-order plot may result from the presence of an impurity.

The cation $(CH_3)_3NBH_2ON(CH_3)_3{}^+$ was surprisingly labile in neutral hot water, and care had to be exercised in recrystallization of its hexafluorophosphate salt.

Discussion

The synthesis of O-bonded cations with chemical properties intermediate between those of the stable bis(tertiary amine)–borane cations and the labile bis(primary amine) cations provides opportunity to investigate reactivity, structure, and reactive intermediates with hydrolysis rates. For the most part, hydrolyses of these cations proceed at measurable rates at experimentally accessible conditions. Because the boron–oxygen bond is normally very strong—one of the most energetic of all single bonds to boron[6]—the chemistry of these new cations could also present some surprises. For example, the thermolysis reaction may lead to new XBH_2O(base) species. Present experience at least supports the idea that the B–O bonds are stronger than the B–N bonds. Attempts to displace pyridine N-oxide with trimethylamine up to 50° have not been successful.

The borane cations derived from the oxide bases form slightly soluble hexafluorophosphates which can be readily recrystallized for purification.

Rates of hydrolytic cleavage of the cations in basic solutions vary in the series; qualitative comparisons are shown in Table III. Results of initial quantitative work with $(CH_3)_3NBH_2OP(CH_3)_3{}^+$ support hydrogen evolution that follows third-order kinetics, second order in hydroxide and first order in cation. The hydrolysis proceeds at a convenient rate in about 0.5 M hydroxide at 29.9°. Contrasted to this is the very low rate of hydrolysis of the very similar cation $(CH_3)_3NBH_2ON(CH_3)_3{}^+$, estimated as 10^{-6} sec^{-1} in 0.9 M sodium hydroxide, yet in hot aqueous solution the latter cation is observed to be degraded while the cation derived from phosphine oxide is stable. If the hydrolytic stability were controlled by the strength of the base–boron bonds, it would be reasonable to expect $(CH_3)_3NBH_2OP(CH_3)_3{}^+$ to be more labile than the nitrogen analog, in keeping with observations that trimethylphosphine oxide is a weaker base than trimethylamine oxide toward sulfur dioxide and possible boron trifluoride.[2,7] Evidently, the greater stability in water and greater lability in base of $(CH_3)_3NBH_2OP(CH_3)_3{}^+$

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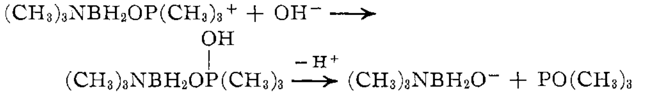
(6) E. L. Muetterties, "The Chemistry of Boron and Its Compounds," John Wiley & Sons, Inc., New York, N. Y., 1967, p 13.

(7) A. B. Burg and J. H. Bickerton, *J. Am. Chem. Soc.*, **67**, 2261 (1945).

require an explanation invoking kinetic rather than thermodynamic parameters. One reasonable explanation for the base-catalyzed hydrolysis of $(CH_3)_3NBH_2OP(CH_3)_3^+$ is primary coordination of hydroxide to phosphorus and then abstraction of a proton



$$(CH_3)_3NBH_2OP(CH_3)_3^+ + OH^- \longrightarrow (CH_3)_3NBH_2O\overset{OH}{\overset{|}{P}}(CH_3)_3 \xrightarrow{-H^+} (CH_3)_3NBH_2O^- + PO(CH_3)_3$$

Fast hydrogen-producing steps would follow. Because the analogous cation $(CH_3)_3NBH_2ON(CH_3)_3^+$ lacks low-lying empty orbitals, this base-catalyzed decomposition would not pertain. The observed second-order dependence on hydroxide could result from an equilibrium process in which there is produced a neutral intermediate, and the rate-controlling step would be the loss of proton. Much more quantitative work and other data are needed before detailed answers to the mechanistic questions can be given. It does appear, however, that there is merit in the early suggestion that borane cations with phosphine bases are sensitive to base because of hydroxyl attack on phosphorus.[8]

Acknowledgment.—Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(8) N. E. Miller and E. L. Muetterties, *J. Am. Chem Soc.*, **86**, 1033 (1964)

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Tetraethylammonium Thiolotrihydroborate

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Tetraethylammonium tetrahydroborate undergoes partial solvolysis in liquid hydrogen sulfide at −78° to produce hydrogen and tetraethylammonium thiolotrihydroborate, $[(C_2H_5)_4N][HSBH_3]$. No further reaction occurs under these conditions. Solid $[(C_2H_5)_4N][HSBH_3]$ suffers slight decomposition upon immediate warming from −78° to room temperature but thereafter only decomposes very slowly. A solution of $[(C_2H_5)_4N][HSBH_3]$ in liquid hydrogen sulfide at −78° reacts very slowly with excess hydrogen chloride to form tetraethylammonium trichlorothioloborate, $[(C_2H_5)_4N][Cl_3BSH]$. A hydrogen sulfide solution of $[(C_2H_5)_4N][HSBH_3]$ rapidly absorbs diborane to produce the unstable compound $[(C_2H_5)_4N][HS(BH_3)_2]$.

Introduction

The chemistry of boron–sulfur compounds has received relatively little attention up to the present time. A recent review of this area by Muetterties[1] reveals that, with the exception of a handful of compounds, most known materials with boron–sulfur bonds are boron sulfide derivatives, alkylthio-substituted organoboranes, or borane adducts of organic sulfides.

The insertion of sulfur into boron hydrides and boron hydride ions is a synthetic problem that should produce a family of new compounds with interesting properties. The presence of lone pairs of electrons on sulfur which are available for dative bonding should have a significant effect on the structure and reactivity of sulfur substituted boranes, while the presence of SH groups on neutral boranes might enable such compounds to behave as proton acids and form novel anions.

In this paper we describe a sulfur derivative of the tetrahydroborate ion, tetraethylammonium thiolotrihydroborate, $[(C_2H_5)_4N][HSBH_3]$, which is prepared by the solvolysis of $[(C_2H_5)_4N]BH_4$ in liquid hydrogen sulfide at −78°.

Experimental Section

General Data.—Volatile compounds were manipulated, separated, and purified with conventional high-vacuum apparatus. Noncondensable gases were collected and measured with an automatic Toepler pump and gas buret. Air-sensitive solids were handled in a polyethylene glove bag flushed with dry nitrogen.

Boron-11 nuclear magnetic resonance (nmr) spectra were obtained with a Varian HA-100 spectrometer equipped with a 32.1-MHz probe and standard accessories; ^{11}B chemical shifts were relative to $(C_2H_5)_2O \cdot BF_3$. Infrared and mass spectra were obtained with a Perkin-Elmer 337 spectrophotometer and a Hitachi Perkin-Elmer RMU-6E spectrometer, respectively.

Reagents.—CP grade hydrogen sulfide was purchased from the Matheson Gas Co., Inc., and was used without further purification. Tetraethylammonium tetrahydroborate was purchased from Alfa Inorganics, Inc., and was recrystallized from 2-propanol before use. Tetraethylammonium tetrahydroborate so prepared gave between 96 and 98% of the expected hydrogen upon acid hydrolysis. Other reagents were prepared and purified by standard methods.

Reaction of $[(C_2H_5)_4N]BH_4$ with Liquid H_2S.—In a typical experiment a Pyrex reaction tube equipped with a high-vacuum stopcock was charged with 0.290 g (2.00 mmol) of $[(C_2H_5)_4N]BH_4$. The vessel was evacuated and cooled to −196°, and sufficient hydrogen sulfide to form 2 ml of solution was condensed in. The vessel was sealed, warmed to −78°, and allowed to stand at this temperature for 24 hr. The tube was then recooled to −196° and opened to the vacuum line, and the evolved hydrogen was collected and found to be present in the amount of 1.92 mmol, corresponding to 96% of that expected for the reaction

$$[(C_2H_5)_4N]BH_4 + H_2S \longrightarrow [(C_2H_5)_4N][HSBH_3] + H_2 \quad (1)$$

The reaction vessel was sealed again and rewarmed to −78°. After 3 days it was recooled to −196° and opened to the vacuum line; less than 0.01 mmol of hydrogen was present.

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(1) E. L. Muetterties in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 10.